Effect of soil moisture content on metribuzin degradation in a sandy soil

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Jebellie, S.J., Prasher, S.O. and Madani, S.A. 1999. **Effect of soil moisture content on Metribuzin degradation in a sandy soil**. Can. Agric. Eng. **41**:221-226. The effects of different soil moisture levels on the degradation of herbicide metribuzin (4-amino-6-[1,1-dimethylethyl]-3-[methylthio]-1,2,4-triazin-5[4H]-one) were investigated under laboratory conditions. Soil typical of southern Quebec, St. Amable sand (Humic Haplorthod), was collected from a field with no history of pesticide application for the previous five years and used in the laboratory experiment. Five volumetric moisture content levels, in triplicate, of 10, 15, 25, 35, and 45% and one air dried soil were used to represent different moisture regimes. Soil samples were collected from all treatments 3, 7, 14, 30, 60, and 90 days after metribuzin application and were analyzed with a gas chromatograph for metribuzin residues. Results indicate that the degradation rate of metribuzin was significantly higher ($P<0.05$) at 25 and 35% soil moisture contents than that at all other moisture levels. The metribuzin decay kinetics were expressed with a first order reaction equation with R^2 values ranging from 0.78 to 0.94 for different moisture levels. The half-life of metribuzin varied from 3 to 17 days at 21 ± 2 °C for different moisture treatments. Shortest half-lives were obtained for soil moisture levels of 25 and 35% and longer half-lives resulted for soil at lower moisture levels and at saturation. Therefore, based on the results of this experiment, it can be concluded that watertable management systems for humid regions which maintain higher soil moisture content in the crop root zone may also be effective in enhancing the quick degradation of metribuzin in sandy soils. Such systems can reduce the risk of metribuzin leaching towards groundwater.

Les effets de niveaux différents d'humidité de terre sur la dégradation d'herbicide metribuzin (4-amino-6-[1,1-dimethylethyl]-3-[methylthio]-1,2,4-triazin-5[4H]-une) était étudié sous des conditions de laboratoire. Souiller typique de du sud Québec, St. Amable sable (Humic Haplorthod), n'était recueilli d'un domaine avec aucune histoire d'application de pesticide pour les précédent cinq années et employait dans l'expérience de laboratoire. Cinq humidité volumétrique niveaux contents, dans le triplicata, de 10, 15, 25, 35, et 45%, et un air séchaient la terre étaient employés représenter des régimes différents d'humidité. Les échantillons de terre étaient recueillis de tous traitements 3, 7, 14, 30, 60, et 90 jours après metribuzin application et étaient analysés avec un Gaz Chromatograph pour metribuzin résidus. Les résultats indiquent que le taux de dégradation de metribuzin était considérablement plus haut ($P<0.05$) à 25 et 35% contenu d'humidité de terre que qu'à tous autres niveaux d'humidité. Le metribuzin pourriture kinetics étaient exprimés avec une première équation de réaction d'ordre, avec R2 valeurs variant de 0.78 à 0.94 pour des niveaux différents d'humidité. La moitié - vie de metribuzin variait de 3 à 17 jours à 21 ± 2°C pour des traitements différents d'humidité. La plus courte moitié - vies étaient obtenues pour des niveaux d'humidité de terre de 25 et 35%, et plus longue moitié - vies résultées pour la terre aux niveaux bas d'humidité et à saturation. Donc, basé sur les résultats de cette expérience, il peut être conclu ces systèmes de gestion de table d'eau pour des régions humides qui entretiennent le contenu plus haut d'humidité de terre dans la zone de racine de récolte, peut aussi être efficace dans la dégradation rapide de metribuzin dans des terres sablonneuses; tels systèmes réduisent le risque de metribuzin leaching vers l'eau de sol.

INTRODUCTION

Metribuzin (4-amino-6-[1,1-dimethylethyl]-3-[methylthio]-1,2,4-triazin-5[4H]-one) is a heterocyclic basic organic molecule ($C_8H_{14}N_4OS$) widely used in pre-emergence and early post-emergence control of annual grasses and numerous broadleaf weeds in potatoes, tomatoes, soybeans, and sugarcane (Colby et al. 1989). The solubility of metribuzin in water and its sorption coefficient (K_{oc}) are 1220 and 60 mL/g, respectively (Wauchope et al. 1992). High water solubility and a low partitioning coefficient indicate metribuzin's low adsorption and relatively high mobility in soil (Savage 1977). This has led to the detection of metribuzin residues in surface and ground waters (Aubin et al. 1993; Shukla et al. 1995).

Metribuzin transport through the root and vadose zones to ground water is affected by several abiotic and biotic processes. Retention (abiotic) and transformation (biotic and abiotic processes) are two important mechanisms that govern the amount of metribuzin available for leaching through the soil profile. For most pesticides, transformation results in detoxification to innocuous products (Somasundaram and Coats 1991). Transformation of pesticides can start immediately after application and may occur through chemical transformation and biological degradation. In chemical transformation, there will be a change in the original compound's structure through various reactions, such as hydrolysis or oxidation (Coats 1991). Depending on soil environmental conditions, biological transformation (degradation) of metribuzin can occur by processes such as oxidation (N-deamination, sulfoxidation) and hydrolysis (demethylthiolation, deamination) (Hatzios and Penner 1988). The soil microbial population is responsible for biological transformations through which pesticides are transformed into smaller fragments and inorganic products like CO_2 and H_2O. This transformation has been reported to follow the power rate model (Zimdahl et al. 1994):

$$\frac{dC}{dt} = -kC^n \qquad (1)$$

Table I. Physical and chemical characteristics of the soil (St. Amable sand).

Soil texture	Sand (%)	Silt (%)	Bulk density (kg/m^3)	Organic matter (%)	pH	CEC* (cmol/kg)	Saturated H.C. (mm/h)
Sand	92.2	4.3	1350	3.5	5.5	4.9	81

* CEC - Cation Exchange Capacity
H.C. - Hydraulic conductivity

where:

C = concentration of pesticide (mg/kg),
k = rate constant (d^{-1}),
t = time (d), and
n = reaction order.

In most cases, metribuzin degradation matches first-order kinetics (Hyzak and Zimdahl 1974; Bowman 1991; Locke et al. 1994). Zimdahl et al. (1994) have obtained highly accurate results with the help of a biexponential equation. Depending on the soil and environmental conditions, the half-life of metribuzin in field soils can range from a few days to four months (Hatzios and Penner 1988).

Biological agents such as bacteria and fungi are known to be the main pesticide degraders. Soil microbial activity is dependent not only on the availability of carbon, nitrogen, and other nutrients but also on aeration, pH, temperature, and soil moisture levels. Each of these factors may affect biological activities. Among the various above-mentioned parameters, soil moisture is considered to be an important stimulant and an essential contributor to the growth of soil microbes. Water influences biological populations in many ways. Microbes use soil moisture as a medium for growth and for cell metabolism. Water also serves in the hydrolysis and hydroxylation reactions of biological compounds.

Transport of microbial nutrients to the cells and waste materials away from them is accomplished by soil moisture. Water also moderates temperature fluctuations in the soil system. The higher the water content, the more resistant that soil ecosystem is to temperature fluctuations (Tate 1995). Therefore, maintaining a higher soil moisture content at root zone depth (possibly through watertable management), encourages microorganism activity and increases the microorganisms use of organic pesticides for nourishment. Thus, under aerobic conditions in the vadose zone, pesticide oxidation usually proceeds first, followed by nitrification, provided that sufficient oxygen still remains (Bitton and Gerba 1984). Studying the effects of soil moisture content on the biodegradation of pesticides is very complex, because the dissipation process usually includes processes such as leaching, plant uptake, volatilization and photodecomposition. Despite metribuzin's extensive use, very few studies have concentrated on the degradation of the substance with respect to different soil moisture contents (Aubin 1994; Jebellie et al. 1996).

This study was undertaken to investigate the effects of different soil moisture levels on the degradation of metribuzin in a sandy soil. Specifically, the study aimed to determine the range of volumetric soil moisture contents at which the greatest

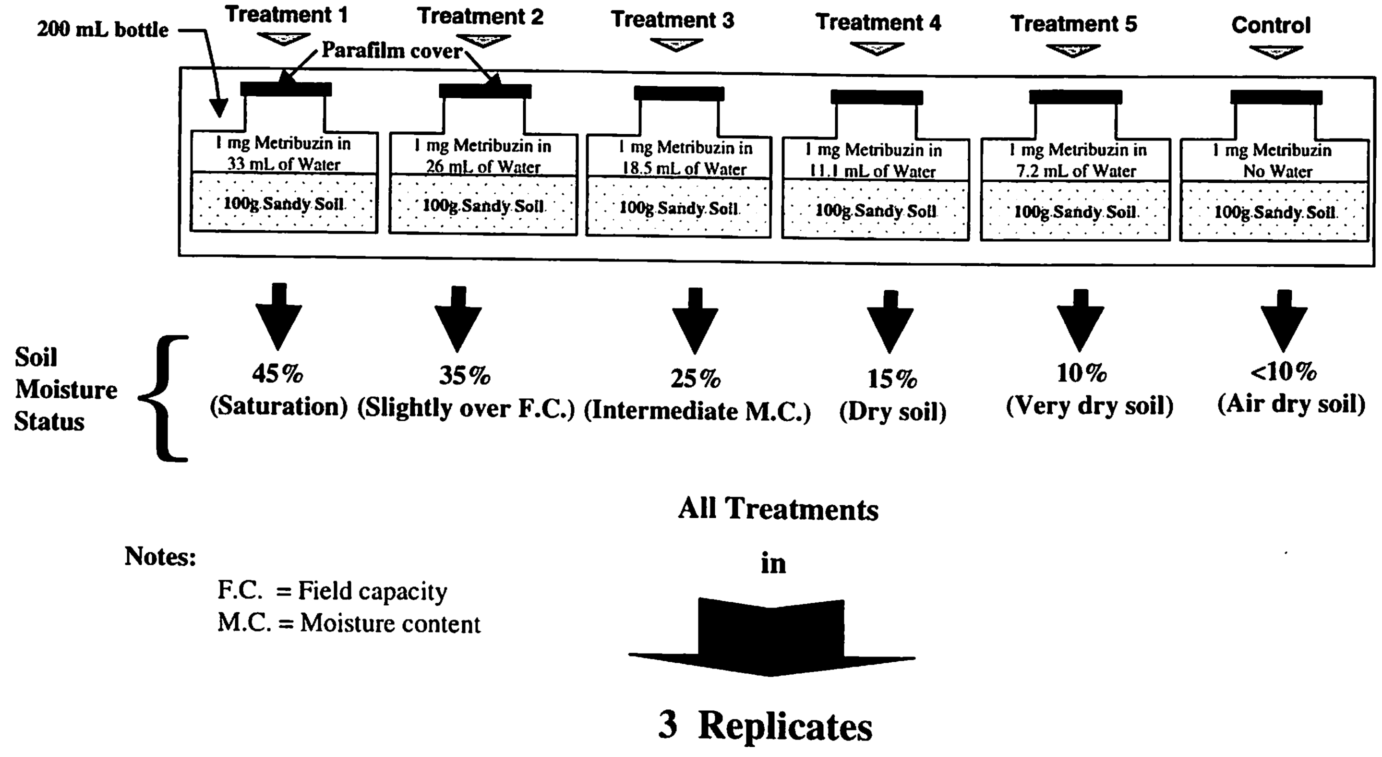

Fig. 1. Experimental plan of kinetic studies for metribuzin degradation.

Table II. General linear models procedure.

(A) Repeated measures analysis of variances for metribuzin
Tests of hypotheses for between-treatments-effects

Source	DF*	Type III SS	Mean square	F	Pr>F
Moisture	5	151.76	30.35	17.15	0.0001
Error	12	21.24	1.77		

Contrast	DF	Contrast SS	Mean square	F	Pr>F
0%-Mois vs 10% Mois	1	9.0	9.0	5.08	0.0436
0%-Mois vs 15% Mois	1	10.34	10.34	5.84	0.0325
0%-Mois vs 25% Mois	1	42.90	42.90	24.23	0.0004
0%-Mois vs 35% Mois	1	55.00	55.00	32.07	0.0001
0%-Mois vs 45% Mois	1	8.41	8.41	4.75	0.0499
10%-Mois vs 15% Mois	1	0.05	0.05	0.03	0.8734
10%-Mois vs 25% Mois	1	12.6	12.6	7.12	0.0205
10%-Mois vs 35% Mois	1	19.51	19.51	11.02	0.0061
10%-Mois vs 45% Mois	1	34.81	34.81	19.66	0.0008
15%-Mois vs 25% Mois	1	11.11	11.11	6.28	0.0276
15%-Mois vs 35% Mois	1	17.64	17.64	9.96	0.0083
15%-Mois vs 45% Mois	1	37.41	37.41	21.13	0.0006
25%-Mois vs 35% Mois	1	0.75	0.75	0.42	0.5271
25%-Mois vs 45% Mois	1	89.30	89.30	50.45	0.0001
35%-Mois vs 45% Mois	1	106.43	106.43	60.12	0.0001

(B) Univariate test of hypotheses for within-treatments-effects

Source: TIME

				Adj Pr>F		
DF	Type III SS	Mean square	F	Pr>F	G-G	H-F
5	378.30	75.66	58.16	0.0001	0.0001	0.0001

Source: TIME*MOISTURE

				Adj Pr>F		
DF	Type III SS	Mean square	F	Pr>F	G-G	H-F
25	56.06	2.24	1.72	0.044	0.0866	0.0440

* DF - degrees of freedom
G-G - Greenhouse-Geisser
H-F - Huynh-Feldt
SS - sum of squares
Adj - adjusted
Pr>F - probability of a value greater than F

amount of metribuzin degradation can be achieved in the soil. The results from this study will help us to better understand the environmental impact of watertable management systems on agricultural farms. With higher soil moisture levels, coupled with higher soil temperatures during the summer months, pesticides may degrade faster, thus, reducing the risk of metribuzin transport to ground water.

MATERIALS and METHODS

Sampling method

The test soil, typical of southern Quebec, St. Amable sand (Ferro-Humic Podzol), was collected from the A horizon of a field with no history of any pesticide application in the previous five years. Table I shows some of the physical characteristics of the soil. To study the degradation of metribuzin, five different soil moisture levels were chosen to reflect the different volumetric moisture contents that might occur during watertable management in the field. The 10% moisture content was used to represent the soil moisture level after a long drought (very dry soil). The 15% moisture content represents soil after a relatively short drought (dry soil). The intermediate soil moisture content is represented by the 25% moisture level. To represent the soil moisture content at slightly higher than field capacity (F.C.) and saturation, 35 and 45% moisture levels were used. Air dried soil was added to the experimental protocol as a control (Fig. 1).

The experimental scheme followed a completely randomized design with three replicates for each treatment. The experiment was carried out in the laboratory at room temperature (21 ± 2°C) in eighteen 200 mL glass bottles. The bottle openings were covered with parafilm to prevent water evaporation. These covers were opened for a few minutes every week to avoid oxygen depletion. Each 200 mL bottle received 100 g of air-dried soil. In addition, 1.0 mg of metribuzin in powdered form (99.9% pure) was dissolved in 1 mL of methanol and added to each bottle to yield a uniform initial concentration of 10 m/kg for all treatments. To bring the bottles' volumetric soil moisture contents to the 10, 15, 25, 35, and 45% levels, they received 7.2, 11.1, 18.5, 26, and 33 mL of tap water, respectively (Fig. 1). The control bottles were treated with metribuzin but did not receive any water. The volume of water required in each bottle was calculated based on the original soil bulk density of 1350 kg/m^3 and mass of soil in each bottle (100 g). For instance, for an intermediate moisture content (25%), the calculation was: (0.25/1.35)100 = 18.5 g. The soil in each bottle was sampled 3, 7, 14, 30, 60, and 90 days after herbicide application.

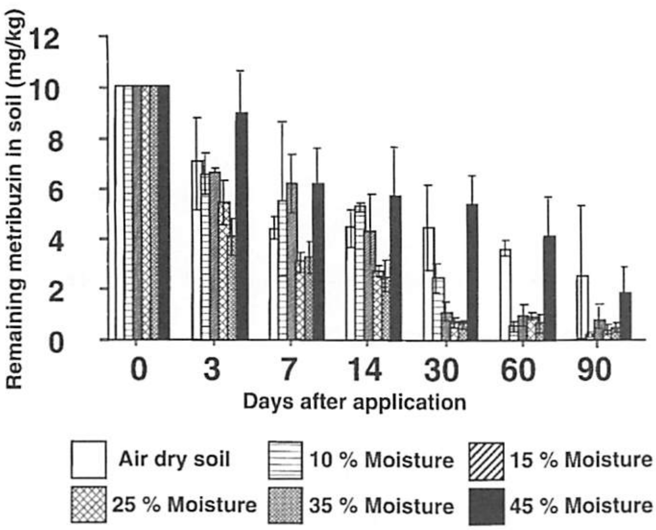

Fig. 2. Remaining concentration of metribuzin in soil; standard deviations are shown with error bars.

Extraction and analysis of metribuzin residues

On each sampling day, 10 g of soil was removed from the bottles. The soil was transferred to a flat-bottom flask where 100 mL of methanol was added and the mixture was shaken for 1 h. The mixture was transferred to a flask and filtered under partial suction. The collected organic phase was evaporated in a rotary evaporator until dry and the dried residues were massed and dissolved in 10 mL of hexane. Extracts were immediately loaded to a gas chromatograph (GC) for analysis.

Sample extracts were analyzed using a gas chromatograph (Model 3400, Varian Inc., St. Laurent, QC). The column was a 0.53 mm i.d., fused silica Megabore DB-5 of 1.5 µm film thickness (J&W Scientific Inc., Folsom, CA). A thermionic specific detector (TSD), also known as nitrogen-phosphorus detector (NPD), was factory-installed by Varian Inc. to detect metribuzin residues. The injector temperature was set at 250°C and the detector was kept at 300°C. The column temperature was maintained at 180°C for 9 min and then the temperature was increased to 200°C at a rate of 4°C/min. At 200°C, the temperature was maintained for one minute and then raised to 280°C at a rate of 20°C/min. The column was kept at this high temperature for 9 min. The detection limit for the soil samples, evaluated by injecting extracts with decreasing herbicide concentrations, was estimated to be 10 µg/kg. The recovery rate was obtained by fortifying 5 g of untreated oven dry soil with 0.05, 0.5, and 5 mg/kg of herbicides. The samples were left to equilibrate for 24 h, after which time they were extracted and analyzed by GC. The recovery rate was estimated to be 88 ± 5%.

Analyses

Pesticide degradation can usually be represented by first-order kinetics. This has been found to be approximately true or at least true enough to cause little loss of accuracy in most studies (Wagenet and Rao 1990). Therefore, a first-order kinetic equation was used in this study to describe the degradation rate of metribuzin at all moisture levels.

A statistical analysis was performed using the SAS program. Since the soil solution samples were taken from the same bottles at predetermined time intervals, the independency of observation and uniformity of sampling variance could not be maintained. In this situation, the classical statistical analysis of variance may not produce reliable results. Thus, the repeated measures analysis of variance was employed instead. The repeated measures analysis of variance was employed to evaluate the effects of various soil moisture contents and their contrasts. In this analysis, the adjusted F test of Huynh-Feldt (H-F) or Greenhouse-Geisser (G-G) was employed to evaluate the effect of treatments and time (Dutilleul and Legendre 1993).

RESULTS and DISCUSSIONS

Table II presents the results of statistical analysis for metribuzin. The effect of "moisture" content on metribuzin degradation is highly significant at the 95% level (P=0.0001). It also shows that the differences between the two moisture levels 25 and 35% vs the air dry and saturation treatments are highly significant. The contrasts between the 10 vs 15% and 25 vs 35% moisture contents were not statistically significant at the 95% level. The results of the univariate test in Table II show that, irrespective of moisture content level, the metribuzin concentration significantly reduced from its original spiked level (H-F = 0.0001) with time. The interaction of time and moisture also had a significant impact (H-F = 0.0440) on the metribuzin concentration.

Figure 2 shows the average metribuzin concentrations remaining in the soil as a function of time. The error bars, representing the average values ± one standard deviation, are also drawn. Metribuzin's background concentration in the soil was found to be negligible. Although metribuzin seems to degrade quite rapidly for all moisture content conditions, the fastest and greatest degradation occurred at the 35 and 25% moisture content levels. The degradation rate was slowest for the saturated soil condition.

First-order kinetics were applied to describe the degradation rate of metribuzin at all moisture levels. The metribuzin decay expression as a function of time, followed the simplified expression:

$$C = k(t)^{-n} \tag{2}$$

where:

C = metribuzin concentration (mg/kg),
k = rate constant (mg kg^{-1} d^{-1}),
t = time after application (d), and
n = reaction order.

Figure 3 gives the fitted values and the related coefficients of determination (R^2) for each soil moisture treatment. Among the fitted curves, that of 35% moisture level samples produced the highest R^2 value (0.95).

Table III shows the metribuzin half-lives with respect to volumetric soil moisture contents. The half-life of metribuzin varied from 3 to 17 days for different moisture levels at 21 ± 2°C. The shorter half-lives were obtained for soil moisture levels of 25 and 35%, and the longer half-lives for lower soil moisture levels and saturation. Metribuzin's half-life at soil saturation (45%) is the longest (17 d). It seems that saturation slowed down the degradation rate of metribuzin in this soil. In

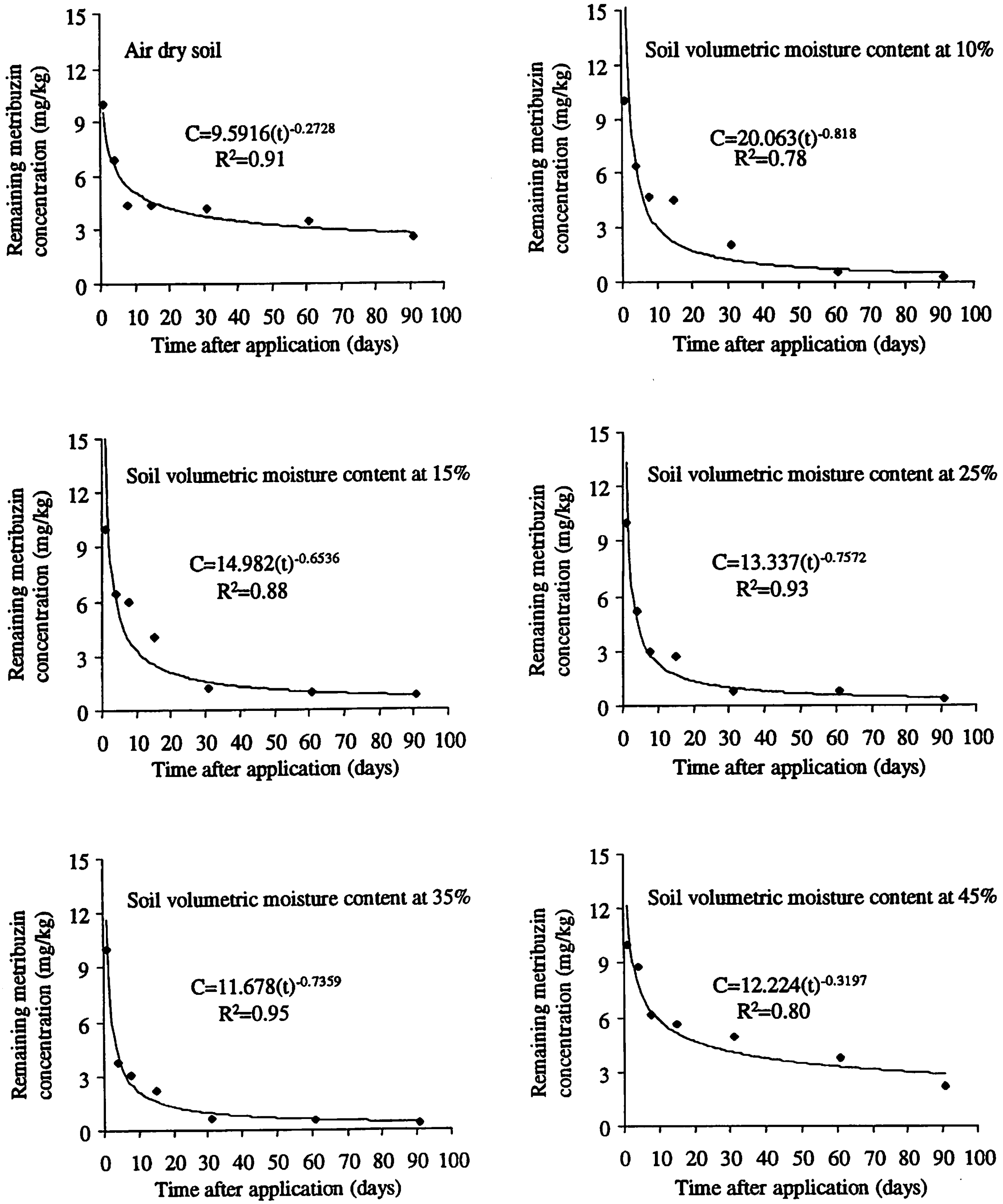

Fig. 3. Fitted vs measured metribuzin concentrations in soil at different moisture levels plotted with time.

the applied metribuzin was degraded in 30 d, while only 47% of the herbicide degraded when exposed to saturated conditions during the same period. As observed from Fig. 3, although metribuzin concentration in most treatments approached zero 90 d after application, the air dry and saturation treatments reduced only to one third of their original spiked level.

Table III. Metribuzin half-life at different volumetric soil moisture contents.

Moisture levels (%)	Half-life (d)
<10 (air dried soil)	12
10 (very dry soil)	6
15 (dry soil)	6
25 (intermediate moisture content)	4
35 (slightly over field capacity)	3
45 (saturated)	17

The study of metribuzin half-life and its order of reaction at different moisture levels helps us to better understand and formulate the metribuzin decay functions within mathematical models that deal with vadose and saturated zones. These laboratory results indicate that the degradation of metribuzin is enhanced at soil moisture levels that are close to or slightly higher than field capacity. Therefore, certain watertable management systems, such as controlled drainage and subirrigation, which tend to maintain higher moisture content in the crop root zone may also increase degradation of metribuzin residues. Further studies are, however, needed to make sure that greater soil moisture contents do not promote more herbicide leaching.

CONCLUSIONS

This study focused on evaluating the effects of different soil moisture levels on the degradation rates of metribuzin in a sandy soil. Five soil moisture content scenarios were simulated: 10, 15, 25, 35, 45%; an air dry soil was used as a control. Results indicate that increasing the soil moisture content to a level close to or slightly higher than field capacity, can significantly reduce metribuzin concentrations and by association the herbicide's half-life. The decay kinetics were best expressed with a first order reaction. R^2 regression values for fitted curves varied from 0.78 to 0.95, with the highest values for the 25 and 35% moisture levels. Studying the half-life and reaction order for metribuzin in different moisture regimes helps us to better understand and formulate metribuzin decay functions within mathematical models pertaining to the fate and transport of herbicides. Considering that a controlled drainage or subirrigation system can maintain moisture contents at these favorable levels within root-zone depths, laboratory results support the possibility that farmlands with these systems can be very effective in enhancing degradation of metribuzin residues in sandy soils. They may also help to reduce the risk of metribuzin leaching towards ground water.

REFERENCES

Aubin, E. 1994. Impact of water table management on groundwater contamination by two herbicides. M.Sc. Thesis. Department of Civil Engineering, McGill University, Montreal, QC.

Aubin, E., S.O. Prasher and R.N. Yong. 1993. Impact of water table on metribuzin leaching. In *Proceedings of the 1993 Joint CSCE-ASCE National Conference on Environmental Engineering*, 548-564. July, Montreal, QC.

Bitton, G. and C.P. Gerba. 1984. *Groundwater Pollution Microbiology*. New York, NY: John Wiley & Sons.

Bowman, B., 1991. Mobility and dissipation studies of metribuzin, atrazine and their metabolites in plainfield sand using field lysimeters. *Environmental Toxicology and Chemistry* 10: 573-579.

Coats, R.J. 1991. Pesticide degradation mechanisms and environmental action. In *Pesticide Transformation Products*, 10-30. ACS Symposium Series 459. Washington, DC: American Chemical Society.

Colby, S.R., E.R. Hill, L.M. Kitchen, R.G. Lym, W.J. McAvoy and R. Prasad. 1989. *Herbicide Handbook of the Weed Science*, 6th ed. Champaign, IL: Weed Science Society of America.

Dutilleul, P. and P. Legendre. 1993. Spatial heterogeneity against heteroscedasticity: an ecological paradigm versus a statistical concept. *Oikos* 66:152-171.

Hatzios, K.K. and D. Penner. 1988. Metribuzin. In *Herbicides, Chemistry, Degradation, and Mode of Action*, eds. P.C. Kearney and D.D. Kaufman, 3: 403.

Hyzak, D.L. and R.L. Zimdahl. 1974. Rate of degradation of metribuzin and two analogs in soil. *Weed Science* 22:75-79.

Jebellie, S.J., S.O. Prasher and R.S. Clemente. 1996. Role of soil moisture content in reducing environmental pollution from pesticides. *Canadian Water Resources* 21(4): 79-87.

Locke, M.A., S.S. Harper and L.A. Gaston. 1994. Metribuzin mobility and degradation in undisturbed soil columns. *Soil Science* 157(5): 279-288.

Savage, K.E. 1977. Metribuzin persistence in soil. *Weed Science* 25:55-59.

Shukla, S., S. Mostaghimi and A.C. Bruggeman. 1995. Impact potential score: a risk assessment technique for pesticide contamination of groundwater. ASAE Paper No. 95-2425. St. Joseph, MI: ASAE.

Somasundaram, L. and J.R. Coats. 1991. Pesticide transport products in the environment. In *American Chemical Society Symposium Series 459*, 2-30. Washington, DC: American Chemical Society.

Tate, R.L. 1995. *Soil Microbiology*. New York, NY: John Wiley & Sons, Inc.

Wagenet, R.J. and P.S.C. Rao. 1990. Modeling pesticide fate in soils. In *Pesticides in the Soil Environment*, ed. H.H. Cheng, 351-399. Madison, WI: Soil Science Society of America, Inc.

Wauchope, R.D., T.M. Buttler, A.G. Hornsby, P.W.M. Augustijn-Beckers and J.P. Burt. 1992. The SCS/ARS/CES pesticide properties database for environmental decision-making. In *Reviews of Environmental Contamination and Toxicology*, ed. G.W. Ware, 31-35. New York, NY: Springer-Verlag Publishers.

Zimdahl, R.L., B.K. Cranmer and W.W. Stroup. 1994. Use of empirical equations to describe dissipation of metribuzin and pendimethalin. *Weed Science* 42 (2): 241-248.